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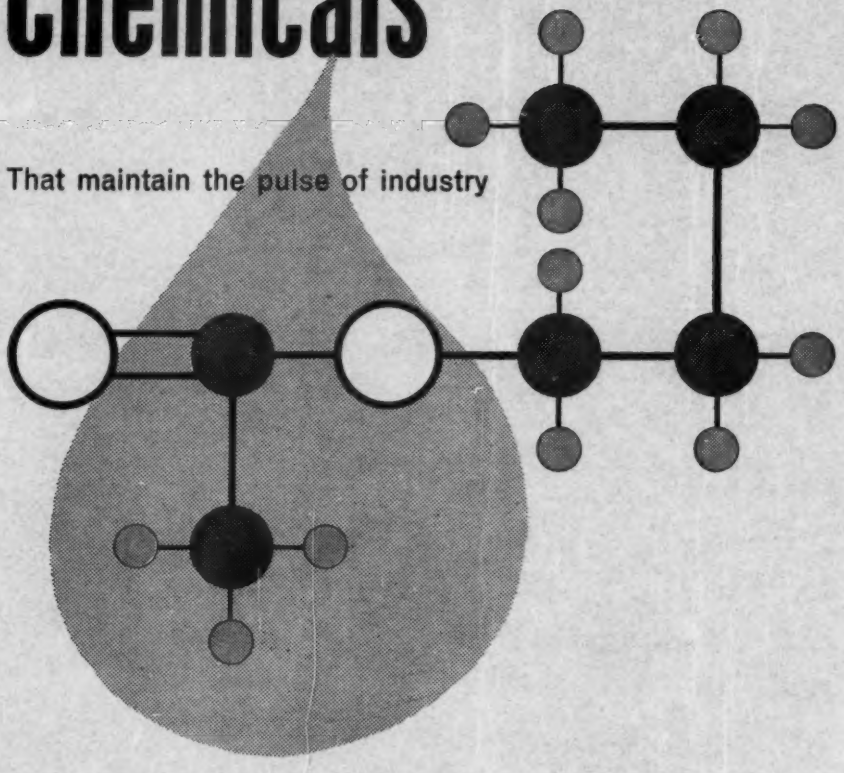

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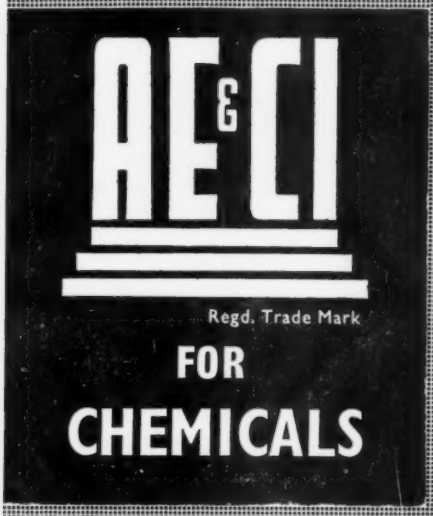

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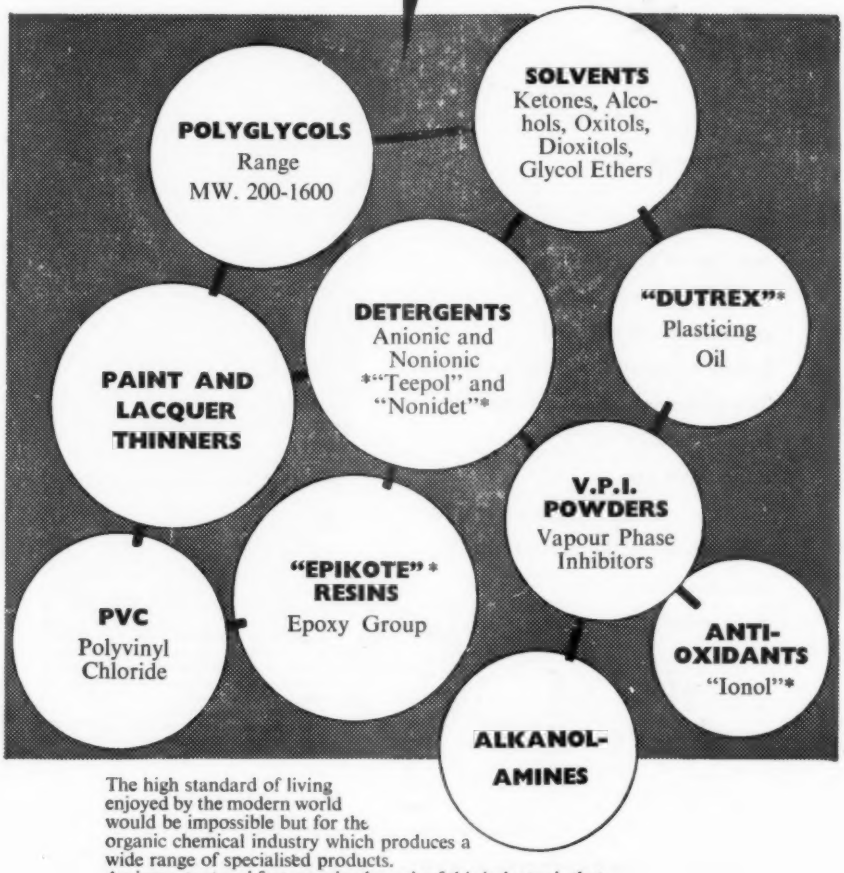

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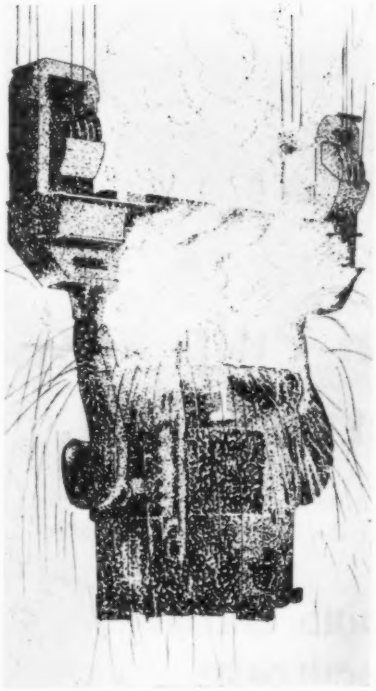

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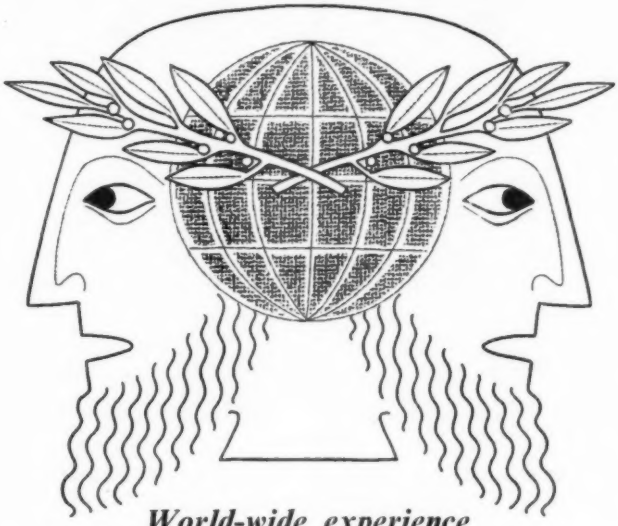

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PREPARATION OF DOUBLE METAL SULPHIDES OF THE TYPE AB_2S_4. PART II. COMPOUNDS OF TIN

by

L. D. C. BOK and J. C. A. BOEYENS

OPSOMMING

Drie dubbelmetaal-sulfides, $SnCu_2S_4$, $BaSn_2S_4$ en $SnAs_2S_4$, sowel as die verbinding Sn_3S_4 is in reaksies in die vaste toestand by betreklik hoë temperatuur berei. $SnCu_2S_4$ het as 'n spinel met a = 10·87Å kristalliseer; die ander verbindinge was tetragonaal.

SUMMARY

Three double metal sulphides, $SnCu_2S_4$, $BaSn_2S_4$, $SnAs_2S_4$ and the compound Sn_3S_4 have been prepared in reactions in the solid state at relatively high temperature. $SnCu_2S_4$ crystallised as a spinel with a = 10.87Å while the other compounds were tetragonal.

In attempting to prepare double metal sulphides containing tin it is important to note the limited range of stability of the three sulphides SnS_2, Sn_2S_3 and SnS. SnS_2 decomposes at 520° to yield Sn_2S_3, which is stable up to 640°. At higher temperatures both yield SnS [1]. That the limits of stability also apply to double metal sulphides based on these binary sulphides was indicated when traces of the 4:2 thiospinel $SnMg_2S_4$ were found after heating the components to 450°, but not after heating to 1000° [2].

EXPERIMENTAL

The preparation of double metal sulphides was attempted by heating the constituent elements, or binary sulphides, in stoichiometric proportions in sealed evacuated tubes (see method (i), Part I [3]). For temperatures up to 500° Pyrex glass tubes were used and "Vitreosil" tubes for higher temperatures.

In attempts to prepare double metal sulphides derived from SnS_2, i.e. $Sn^{IV}M_2^{II}S_4$, mixtures were heated to temperatures between 450 and 500°. For compounds $M^{II}Sn^{III}{}_2S_4$, derived from Sn_2S_3, heating was carried out to 600° and for compounds $M^{IV}Sn^{II}{}_2S_4$ and $Sn^{II}M^{III}{}_2S_4$ the mixtures were kept at 800°.

RESULTS

Systems derived from SnS_2. Sn-Cu-S. Heating of the elements in proportion for $SnCu_2S_4$ for two weeks at 450-500° gave a grey product with a metallic lustre. The X-ray pattern, using a copper target, had 15 measurable lines. All of these, with the exception of one with estimated intensity 1, could be indexed for a spinel with a = 10·87Å, as shown in Table I.

TABLE I

Index	Intensity (Estimated)	Spacing d (Å)	$\sin^2\theta$ Expt.	$\sin^2\theta$ Calc.
311	9	3·151	0·0597	0·0553
400	4	2·728	0·0797	0·0804
	1	2·612	0·0870	
440	10	1·919	0·1609	0·1608
531	3	1·842	0·1746	0·1759
622	8	1·639	0·2204	0·2211
444	2	1·568	0·2410	0·2412
800	6	1·357	0·3216	0·3216
662	7	1·246	0·3815	0·3819
844	8	1·100	0·4815	0·4824
864	7	1·046	0·5825	0·5822
880	3	0·960	0·6438	0·6432
10,62	8	0·918	0·7034	0·7035
12,40	6	0·859	0·8034	0·8040
10,66	5	0·829	0·8628	0·8632

Other Systems derived from SnS_2. Results are summarised in Table II. In each case the preparation was attempted by heating for two weeks at 450-500°.

TABLE II

Attempted Compounds	Products Identified[4]
$SnBe_2S_4$	Binary Sulphides
$SnZn_2S_4$	α—Zns, β—ZnS, SnS, SnS_2.
$SnCa_2S_4$	SnS_2, CaS, SnS.
$SnTi_2S_4$	SnS_2, Ti_2S_3, SnS, TiS_2.
$SnBa_2S_4$	SnS_2, SnS, Sn_2BaS_4.
$SnHg_2S_4$	HgS, SnS_2.
$SnPb_2S_4$	Binary Sulphides
$SnCd_2S_4$	α—CdS, β—CdS, Sn_3S_4, SnS_2
$SnNi_2S_4$	Binary Sulphides
$SnFe_2S_4$	SnS_2, $Fe_{x-1}S_x$ (Pyrrhotite-magnetic)
$SnCo_2S_4$	SnS_2, Sn_2S_3, Co_3S_4

Systems derived from Sn_2S_3. *Sn-BaS-S*. A mixture in proportion for $BaSn_2S_4$ was heated to 600° for two weeks. The X-ray pattern of the black product could be indexed for a tetragonal structure (a=5·50Å, c=8·13Å, c/a=1·478) as in Table III (Cu radiation).

Sn-Sn-S. A mixture of tin powder and sulphur in proportion for Sn_3S_4 was heated to 600° for two weeks. A few lines in the X-ray pattern of the greyish black product could be attributed to the formation of SnS, but the great majority indicated the formation of a tetragonal compound with a=7·553Å, c=8·383Å, c/a=1·11. When a similar mixture was heated to 450° for two weeks the same X-ray pattern was obtained, but heating to 800° gave SnS as the product. Some Sn_3S_4 was, however, formed when a mixture in proportion for $SnCo_2S_4$ was heated to 800° for two weeks. The X-ray pattern for Sn_3S_4 is given in Table IV (Co target).

Other Systems derived from Sn_2S_3. Results are summarised in Table V. In each case heating was carried out for two weeks at 600°.

Systems derived from SnS. No compound of the type $M^{IV}Sn^{II}{}_2S_4$ was obtained by heating the constituents to 800°. The results are summarised in Table VI.

TABLE III

Index	Intensity (Estimated)	Spacing d (Å)	$\sin^2\theta$ Expt.	$\sin^2\theta$ Calc.
200	7	3·399	0·0514	0·0496
211	1	2·873	0·0718	0·0710
202	8	2·657	0·0840	0·0856
220	5	2·440	0·0996	0·0992
300	3	2·318	0.1103	0·1116
004	1	2·021	0·1452	0·1440
223	10	2·819	0·1793	0·1802
401	4	1·679	0·2104	0·2104
331	1	1·590	0·2343	0·2322
224	5	1·554	0·2455	0·2432
215	6	1.433	0·2887	0·2880
333	6	1·413	0·3014	0·3042
503	3	1·233	0·3900	0·3910
513	5	1·214	0·4021	0·4034
530	1	1·183	0·4238	0·4216
600	3	1·154	0·4452	0·4464
443	2	1·116	0·4768	0·4778
620	5	1·091	0·4986	0·4960
540	6	1·080	0·5084	0·5084
720	5	0·949	0·6592	0·6572
642	1	0·933	0·6815	0·6808
730	5	0·907	0·7213	0·7202
514	5	0·881	0·7643	0·7634
229	5	0·847	0·8270	0·8282
645	5	0·825	0·8709	0·8698
00,10	1	0·812	0·9007	0·9000
823	5	0·803	0·9214	0·9242
448	3	0·782	0·9712	0·9728
663	5	0·780	0·9754	0·9738
726	2	0·778	0·9806	0·9812

TABLE IV

Index	Intensity (Estimated)	Spacing d (Å)	$\sin^2\theta$ Expt.	$\sin^2\theta$ Calc.	A.S.T.M.[4] for SnS d	I/I_1
110	5	5·363	0·0278	0·0281		
002	6	4·166	0·0461	0·0456		
200	1	3·683	0·0589	0·0562		
201	3	3·434	0·0679	0·0676		
112	4	3·285	0·0741	0·0737		
211	2	3·139	0·0812	0·0819		
	1	2·934	0·0929		2·93	32
003	10	2·797	0·1023	0·1026		
220	5	2·666	0·1125	0·1124		
310	2	2·378	0·1415	0·1405		
311	3	2·303	0·1508	0·1519	2.30	32
203	5	2·247	0·1583	0·1588		
213	1	2·112	0·1799	0·1829		
321	3	2·029	0·1942	0·1941		
	3	1·991	0·2019		1·99	24
223	7	1·930	0·2146	0·2150		
303	4	1·871	0·2284	0·2291		
330	4	1·777	0·2530	0·2529		
420	4	1·690	0·2800	0·2810		
105	3	1·633	0·2998	0·2991		
	4	1·549	0·3331			
	1	1·447	0·3815		1·45	20
520	6	1·400	0·4080	0·4075		
414	6	1·377	0·4218	0·4213		
441	2	1·320	0·4592	0·4610		
530	2	1·297	0·4747	0·4777		
600	4	1·261	0·5038	0·5058		
007	5	1·195	0·5604	0·5604		
621	2	1·182	0·5727	0·5734		
207	6	1·138	0·6176	0·6166		
631	2	1·116	0·6425	0·6437		
416	2	1·110	0·6497	0·6493		
426	3	1·076	0·6913	0·6914		

TABLE V

Attempted Compound	Products Identified
$MgSn_2S_4$	Binary Sulphides
$CaSn_2S_4$	Sn_2S_3, SnS_2, SnS
$BeSn_2S_4$	Binary Sulphides
$HgSn_2S_4$	HgS, Sn_2S_3, SnS
$PbSn_2S_4$	Sn_2S_3, SnS_2, SnS, PbS
$CuSn_2S_4$	CuS, SnS_2, SnS
$ZnSn_2S_4$	β–ZnS, Sn_2S_3
$CdSn_2S_4$	Sn_2S_3, α–CdS
$NiSn_2S_4$	Binary Sulphides
$CoSn_2S_4$	Sn_2S_3, CoS, Co_2S_4
$TiSn_2S_4$	Binary Sulphides

TABLE VI

Attempted Compound	Period of Heating Hours	Products Identified
$ZrSn_2S_4$	24	Binary Sulphides
$AuSn_2S_4$	12	SnS, SnS_2, Au
$TiSn_2S_4$	24	Binary Sulphides
WSn_2S_4	12	WS_2, W, SnS, SnS_2
$MoSn_2S_4$	12	MoS_2, SnS, SnS_2
$TaSn_2S_4$	24	TaS_2, SnS
$MnSn_2S_4$	24	Binary Sulphides
$FeSn_2S_4$	18	SnS, $Fe_{x-1}Sn_x$ (Pyrrhotite magnetic)

Two compounds of the type $Sn^{II}M^{III}{}_2S_4$ were attempted.

Sn-As$_2$*S*$_3$*-S*. A mixture in the proportions for $SnAs_2S_4$ was heated for 18 hours at 800°. The greyish-white product gave an X-ray pattern which corresponded to that of a tetragonal compound with a=4·734Å, c=3·199Å, a/c=2·337. Details are given in Table VII.

TABLE VII

Index	Intensity (Estimated)	Spacing d (Å)	$\sin^2\theta$ Expt.	$\sin^2\theta$ Calc.	Radiation
110	6	3·358	0·0709	0·0715	Co $K\alpha_1$
101	8	2·653	0·1136	0·1145	,,
200	4	2·373	0·1421	0·1430	,,
111	2	2·317	0·1489	0·1502	,,
211	10	1·762	0·2576	0·2575	,,
220	5	1·673	0·2855	0·2860	,,
002	5	1·607	0·3095	0·3096	,,
310	6	1·500	0·3555	0·3575	,,
112	7	1·437	0·3875	0·3861	,,
301	7	1·415	0·3995	0·4005	,,
202	4	1·321	0·4585	0·4567	,,
321	6	1·214	0·5431	0·5435	,,
400	1	1·183	0·5716	0·5720	,,
222	6	1·153	0·6012	0·6001	,,
330	2	1·115	0·6436	0·6435	,,
312	7	1·091	0·6721	0·6721	,,
411	7	1·080	0·6857	0·6865	,,
420	4	1·058	0·7148	0·7150	,,
103	4	1·035	0·7461	0·7437	,,
213	8	0·950	0·8875	0·8867	,,
500	3	0·947	0·8915	0·8938	,,
510	3	0·929	0·9273	0·9273	,,
510	1		0·9319	0·9299	Co $K\alpha_2$
332	6	0·914	0·9569	0·9569	Co $K\alpha_1$
332	3		0·9616	0·9593	Co $K\alpha_2$
501	8	0·908	0·9700	0·9712	Co $K\alpha_1$
501	4		0·9745	0·9737	Co $K\alpha_2$

Sn-Co-S. A mixture in the proportions for $SnCo_2S_4$ was heated to 800° for two weeks. The product contained Sn_3S_4, CoS_2, CoS and SnS.

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THE REACTION OF 2,4-DINITROBENZENESULPHENYL CHLORIDE WITH STYRENE

by

F. KALUZA and G. W. PEROLD

OPSOMMING

Wanneer 2,4-dinitrobenseensulfenielchloried met stireen in asynsuur reageer, ontstaan naas die verwagte adduk as hoofproduk ook nog (2-asetoksie-2-feniel-etiel)-(2,4-dinitrofeniel)-sulfied. Laasgenoemde produk ontstaan egter nie deur solvolise van die adduk nie. Die reaksie-meganisme word nagegaan. Dieselfde uitgangstowwe in aanwesigheid van water lewer die ooreenkomstige (2-hidroksie-2-feniel-etiel)-(2,4-dinitrofeniel)-sulfied.

SUMMARY

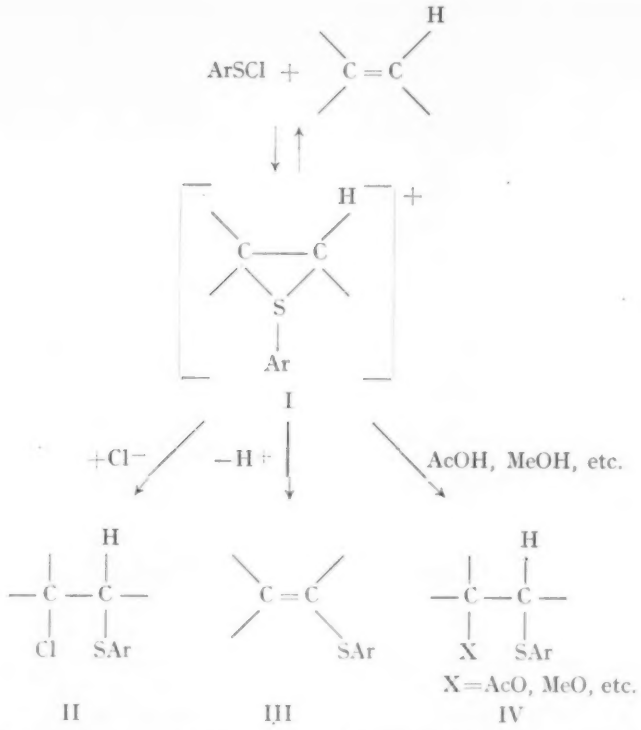
Reaction of 2,4-dinitrobenzenesulphenyl chloride with styrene in acetic acid gives the expected adduct in high yield, together with 2-acetoxy-2-phenylethyl 2,4-dinitrophenyl sulphide. The latter product is however shown not to be formed by solvolysis of the main product. The reaction mechanism is investigated. The same reagents in the presence of water yield the corresponding 2-hydroxy-2-phenylethyl 2, 4-dinitrophenyl sulphide.

2,4-Dinitrobenzenesulphenyl chloride was introduced by Kharasch[1] as a useful reagent for the characterisation of olefines[1] and aromatic hydrocarbons[2]. It had previously also been suggested by Billman[3] as a good reagent for the formation of derivatives of primary and secondary amines. A review of the reactions and uses of this sulphenyl chloride is available[4]. In its application to the characterisation of unsaturated compounds, it has been used for differentiating between closely related olefines [1, 5] and has been successfully used in these laboratories[6] for the characterisation of a series of arylated olefines. The corresponding bromide was here found to be of similar applicability[6].

The main reaction with unsaturated centres is simple addition of the reagent, in the form $ArS^{\delta+} \ldots Cl^{\delta-}$, to yield predominantly normal[1] Markownikoff adducts (II). By-products are the substituted olefines (III) formed by elimination of hydrogen chloride and, in the case of some specifically activated styrenes such as anethole[1] and its simpler analogue p-methoxystyrene[7], products (IV) resulting from solvolysis at the site of the chlorine atom.

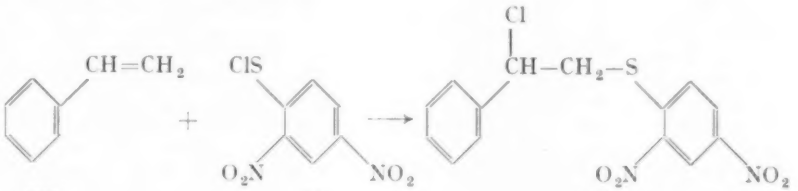
The reactions are in all cases best formulated[8] as proceeding *via* a cyclic sulphonium ion (I) which then either adds chloride ion to yield the normal adduct (II), expels a proton to give the substituted olefine (III) or solvolyses as shown to the products (IV).

In careful studies in our laboratories of mixtures of not specifically activated arylated olefines containing styrene, high yields of the expected adduct (VII) were regularly obtained. An anomalous product was, however, also encountered and the reaction of unsubstituted styrene with 2,4-dinitrobenzenesulphenyl chloride (V) was therefore studied in greater detail. This was particularly necessary in order to allow the certain and unambiguous use of the reagent as an analytical tool, so that clear-cut deductions may be made from the reaction products found in various cases.



II III IV

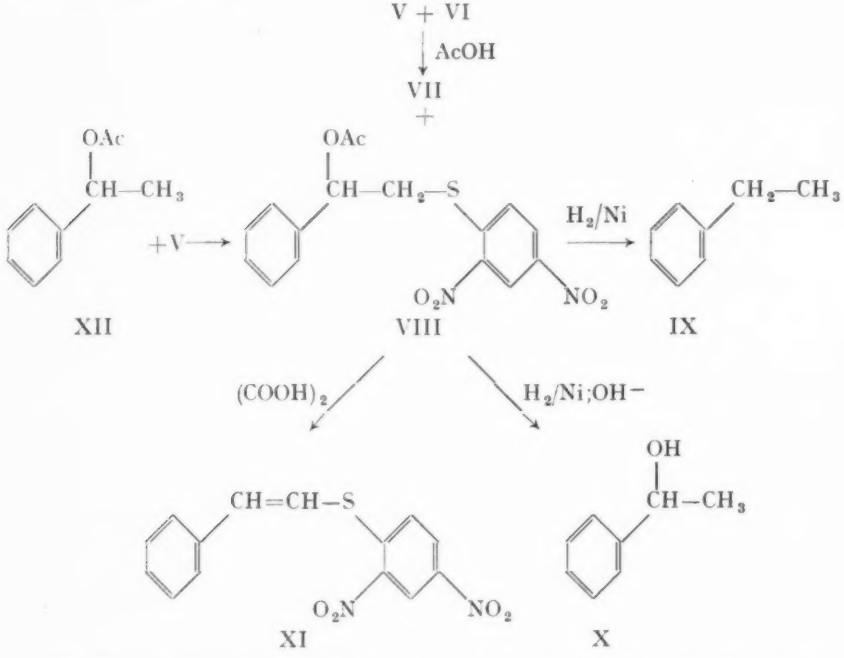
Kharasch[9] found that in this reaction, carried out in dry acetic acid, the reagent added quantitatively to styrene and that only a single product, the expected 2-chloro-2-phenylethyl 2,4-dinitrophenyl sulphide (VII) was obtained in over 90 *per cent* yield. The kinetic data confirmed that the sulphonium ion (type I) was probably an intermediate and that its rate of formation was the rate-determining step in the addition reaction. This course of the reaction was confirmed in a subsequent study on adduct formation with cyclohexene[10].



VI V VII

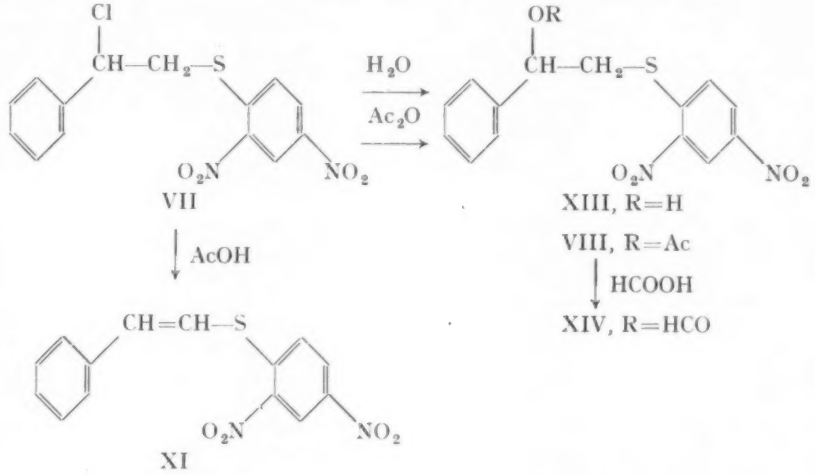
On repeating this reaction with the reactants in stoichiometric proportion, we regularly obtained the adduct (VII) in 95 *per cent.* yield, at room temperature both in sunlight and in darkness, together with a small but reproducible yield (4 *per cent.*) of the unexpected product, $C_{16}H_{14}N_2O_6S$, m.p. 114°. This was shown to be 2-acetoxy-

2-phenylethyl 2,4-dinitrophenyl sulphide (VIII) by the analytical determination and characterisation of the acetoxy group, by the smooth elimination of acetic acid with formation of β-styryl 2,4-dinitrophenyl sulphide (XI) which occurred on heating the new compound with oxalic acid, by hydrogenolysis to ethylbenzene (IX) and by reduction and hydrolysis to 1-phenylethanol (X). The structure (VIII) was confirmed by synthesis by direct reaction of 1-phenylethyl acetate (XII) with 2,4-dinitrobenzenesulphenyl chloride (V).

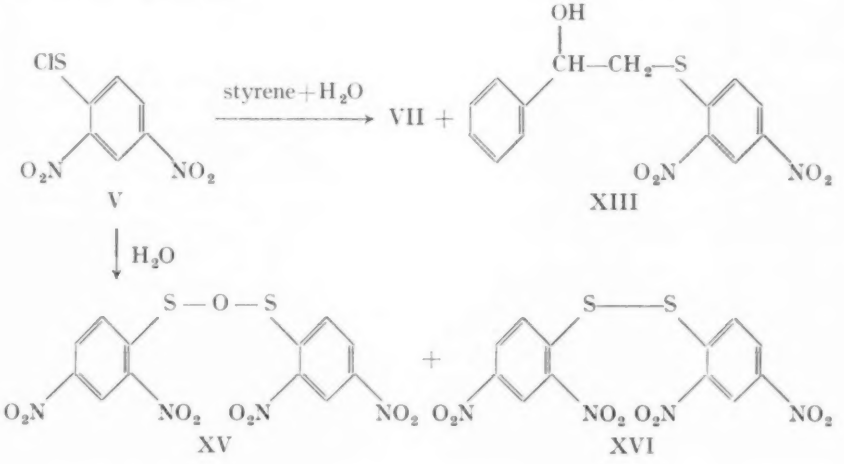


The last-mentioned synthesis, carried out in acetic acid, is interesting in that it is not immediately comparable with the direct substitution of activated hydrogen as in the reaction of acetophenone or acetone with a sulphenyl chloride[11]; furthermore, the reaction does not seem to follow the alternatively expected route, *viz.* elimination of acetic acid from (XII) to give styrene followed by addition of the sulphenyl chloride (V) and solvolysis of the chlorine atom of the adduct (VII). While a small amount of the chloro sulphide (VII) is formed in this reaction by addition of the reagent to secondarily formed styrene, this is clearly a by-product. This could be shown in separate experiments in which solvolysis of this chlorine atom was readily attained either in acetic anhydride to yield the acetoxy sulphide (VIII) or in aqueous dioxane (with or without added silver oxide) to give the corresponding hydroxy sulphide (XIII); this hydroxy sulphide readily afforded the acetoxy sulphide on acetylation in pyridine. While the acetoxy sulphide (VIII) was synthesised in in good yield from 1-phenylethyl acetate (XII), only traces of (VIII) were found in the direct acetolysis of the chloro sulphide (VII) in refluxing acetic acid. The main reaction product in this case was the styryl sulphide (XI), so that acid-catalysed elimination predominated here. Support for this concept was provided by solvolysis

of the acetoxy sulphide (VIII) in formic acid, when the formyloxy sulphide (XIV) was readily obtained. These solvolytic reactions probably again involve a cylic sulphonium ion of type I, as has been shown[1,2] to be likely for solvolyses of the chloro sulphides resulting from the addition of 2,4-dinitrobenzenesulphenyl chloride to propylene, the *cis*- and *trans*-2-butenes and cyclohexene. The mechanism of the formation of the acetoxy sulphide (VIII) from 1-phenylethyl acetate is still under study.



The formation of the acetoxy sulphide (VIII) from 2,4-dinitrobenzenesulphenyl chloride and styrene in acetic acid solution therefore occurs, as in the case of specifically activated styrene derivatives[1,7], by way of addition of acetic acid to the intermediate cyclic sulphonium ion and not through solvolysis of the main product, the chloro sulphide (VII).



A similar reaction course was now furthermore found for the reaction of 2,4-dinitrobenzenesulphenyl chloride with styrene in hydrocarbon solvent medium in the presence of water. The direct hydrolysis of the sulphenyl chloride has been shown to proceed in fast reaction to 2,4-dinitrobenzenesulphenic anhydride (XV) and *bis*-(2,4-dinitrophenyl) disulphide (XVI) as the main products[13]. Reaction of the sulphenyl chloride with water in the presence of styrene as above, however, in addition to the normal adduct as the main product gave the hydroxy sulphide (XIII) in reasonable yield. The reaction is therefore considered to proceed by way of addition of water to the intermediate cyclic sulphonium ion (type I). With regard to the facility with which the direct hydrolysis of the sulphenyl chloride occurs, this reaction therefore demonstrates the rapid rate of formation of the intermediate cyclic sulphonium ion.

EXPERIMENTAL

All m.p.s are corrected

2-Chloro- (VII) and 2-acetoxy-2-phenylethyl 2,4-dinitrophenyl sulphide (VIII). 2,4-Dinitrobenzenesulphenyl chloride (9·26 g.) was dissolved in freshly distilled pure styrene (4·11 g.) and glacial acetic acid (30 ml.) and the mixture kept in sunshine for 7·5 hours. Crystals of the adduct (VII) soon formed and were filtered off (12·37 g., m.p. 142-143°) after standing over night. Crystallisation from acetic acid gave the pure chloro sulphide (VII) as yellow needles, m.p. 143-143·5° (Found: C, 49·8; H, 3·4; Cl, 10·2; N, 8·3; S, 9·7. Calcd. for $C_{14}H_{11}N_2O_4SCl$: C, 49·6; H, 3·3; Cl, 10·5; N, 8·3; S, 9·5%).

The filtrate was diluted with benzene, washed neutral with water and the dried residue (1·038 g.) chromatographed over silica gel (20 g.) in benzene to give the remainder of the chloro sulphide (VII) (345 mg., m.p. 142-143°; total yield, 12·72 g., 95·3 *per cent.*). Benzene:ether (1:1) eluted the acetoxy sulphide (VIII) (600 mg., 4·2 *per cent.*, m.p. 113-113·5°) crystallising from acetone:ethanol as bright yellow prisms, m.p. 114° (Found: C, 53·25; H, 3·8; N, 7·8; S, 8·6. Calcd. for $C_{16}H_{14}N_2O_6S$: C, 53·0; H, 3·9; N, 7·7; S, 8·85%). The infra-red spectrum in potassium bromide dispersion showed the characteristic[14] acetate C-O stretching vibration at 1244 cm^{-1}.

The same reaction in total darkness under identical conditions of working up yielded 95·2 *per cent.* of the chloro sulphide (VII) and 4·0 *per cent.* of the acetoxy sulphide (VIII).

Determination of the acetoxy group in 2-acetoxy-2-phenylethyl 2,4-dinitrophenyl sulphide (VIII). The acetoxy group was transesterified by slow distillation of the acetoxy sulphide (VIII) (263 mg.) with *p*-toluenesulphonic acid (2·5 g.) in ethanol (25 ml.) while gradually adding more ethanol (50 ml.) The distillate on saponification with excess alkali consumed 8·8 ml. 0·1 N NaOH (calcd. 7·3 ml.). The neutral solution was refluxed for 4 hours with *p*-bromophenacyl bromide (370 mg.) and the crude product (360 mg.) chromatographed twice on silica gel (10 g.). Unchanged reagent (135 mg.) was eluted with benzene:light petroleum (1:1) and was followed by *p*-bromophenacyl acetate (149 mg., 85 *per cent.* yield, m.p. 84-85°). Crystallisation from benzene:light petroleum gave the pure compound, m.p. and mixed m.p. 85° (Found: C, 46·95; H, 3·45; Br, 31·1. Calcd. for $C_{10}H_9BrO_3$: C, 46·7; H, 3·5; Br, 31·1%).

Elimination of acetic acid from the acetoxy sulphide (VIII). The acetoxy sulphide (above, 1·087 g.) and anhydrous oxalic acid[16] (2·4 g.) were heated in an oil bath at 150-160° in a slow stream of dry air for 45 mins. The residue in benzene solution was washed neutral with water, recovered (910 mg.) and chromatographed on silica gel (30 g.) in benzene:light petroleum (1:1) to yield β-styryl 2,4-dinitrophenyl sulphide

(XI) (625 mg., 69 *per cent.* yield, m.p. 170-172°). Recrystallisation from benzene gave m.p. 174°, undepressed by an authentic specimen[17] (Found: C, 55·8; H, 3·65; N, 9·2. Calcd. for $C_{14}H_{10}N_2O_4S$: C, 55·6; H, 3·3; N, 9·3%).

Reductive cleavage of 2-acetoxy-2-phenylethyl 2,4-dinitrophenyl sulphide (VIII). The acetoxy sulphide (VIII) (4·0 g.) was hydrogenated over Raney nickel (18 g.) in methanol (150 ml.) at near atmospheric pressure until hydrogen uptake ceased at 9·1 moles/mole compound. The solution was decanted, the catalyst washed out with ether and the combined extracts washed with 2N hydrochloric acid and water to remove basic products. The residue (1·0 g.) obtained from the dried extract was distilled into two fractions. The first (314 mg., b.p. 76-86° (bath)/47 mm.) was redistilled to give pure ethylbenzene (255 mg., b.p. 130°/652 mm.) (Found: C, 90·3; H, 9·8. Calcd. for C_8H_{10}: C, 90·5; H, 9·5%). The *o*-carboxybenzoyl derivative was prepared[18] and had m.p. and mixed m.p. 123° (Found: C, 75·4; H, 5·55. Calcd. for $C_{16}H_{14}O_3$: C, 75·6; H. 5·55%).

The second fraction (586 mg., b.p. 122-126° (bath)/29 mm.) was hydrolysed in aqueous alcoholic 'otassium hydroxide to give 1-phenylethanol (b.p. 120° (bath)/27 mm.) (Found: C, 78·3; H, 8·3. Calcd. for $C_8H_{10}O$: C, 78·65; H, 8·25 %). The phenylurethane had m.p. and mixed m.p. 191·5-192° (Found: C, 74·6; H, 6·3; N, 5·9. Calcd. for $C_{15}H_{15}NO_2$: C, 74·7; H, 6·3; N, 5·8%).

2-Acetoxy-2-phenylethyl 2,4-dinitrophenyl sulphide (*VIII*) *from 1-phenylethyl acetate.* 1-Phenylethyl acetate (1·53 g.) and 2,4-dinitrobenzenesulphenyl chloride (2·3 g.) in glacial acetic acid (20 ml.) were refluxed for 4 hours. β-Styryl 2,4-dinitrophenyl sulphide (XI) crystallised from the reaction mixture (515 mg., m.p. and mixed m.p. 174°). The filtrate was worked up as in the first experiment and chromatographed on silica gel (62 g.) to yield successively a further amount of β-styryl 2,4-dinitrophenyl sulphide (195 mg.), some 2-chloro-2-phenylethyl 2,4-dinitrophenyl sulphide (485 mg., m.p. 140-142·5°, undepressed by the reference compound) and the acetoxy sulphide (VIII) (2·21 g., 66 *per cent.* yield, m.p. 112-113°). Crystallisation from acetic acid and then from acetone gave the pure acetoxy sulphide (VIII), m.p. 114° (Found: C, 52·9, 53·0; H, 3·7, 3·9; N, 7·7; S, 8·65. Calcd. for $C_{16}H_{14}N_2O_6S$: C, 53·0; H, 3·9; N, 7·7; S, 8·85%).

2-Acetoxy-2-phenylethyl 2,4-dinitrophenyl sulphide from the chloro sulphide (*VII*). The chloro sulphide (VII) (15·38 g.) in acetic anhydride (40 ml.) was refluxed for 1 hour, unchanged starting material (6·03 g., m.p. 143°) crystallising on cooling to room temperature. After decomposing the acetic anhydride in the filtrate with water, this was worked up as before to give a residue (9·3 g.) which was chromatographed on silica gel (93 g.) to give further unchanged starting material (3·05 g.), followed by the acetoxy sulphide (VIII) (5·63 g., 34 *per cent.* yield, m.p. 113·5-114°). On extending the reaction period to 7·5 hours, the acetoxy sulphide was obtained in 56 *per cent.* yield. Crystallisation from acetone:ethanol gave the pure compound (VIII), m.p. and mixed m.p. 114° (Found: C, 52·8; H, 4·0; N, 7·7; S, 8·8. Calcd. for $C_{16}H_{14}N_7O_8S$: C, 53·0; H, 3·9; N, 7·7; S, 8·85%).

2-Hydroxy-2-phenylethyl 2,4-dinitrophenyl sulphide (*XIII*) *from the chloro sulphide* (*VII*). The chloro sulphide (VII) (5·0 g.) in dioxane (50 ml.) and water (10 ml.) was refluxed for 16 hours. On cooling, the hydroxy sulphide (XIII) crystallised (3·54 g., 75 *per cent.* yield, m.p. 134-134·5°). The filtrate was worked up and chromatographed in benzene on silica gel (28 g.) as before to yield unchanged starting material (740 mg., 15 *per cent.* recovery, m.p. 142-143°) followed by a further quantity of the hydroxy sulphide (XIII) (480 mg., 10 *per cent.* yield, total yield 85 *per cent.*, mp. 134·5-135°) on elution with ether. Crystallisation from benzene gave the pure hydroxy sulphide,

m.p. 134·5-135° (Found: C, 52·5; H, 3·9; N, 8·8; S, 9·9. Calcd. for $C_{14}H_{12}N_2O_5S$: C, 52·5; H, 3·8; N, 8·75; S, 10·0%).

The hydroxy sulphide (XIII) was also obtained when the chloro sulphide (VII) (5 g.) was shaken with the moist silver oxide obtained from silver nitrate (5 g.) in dioxane (30 ml.) for 3 hours (1.065 g., 23 *per cent.* yield, m.p. and mixed m.p. 134°).

The hydroxy sulphide (XIII) (309 mg.) in acetic anhydride (1·5 ml.) and pyridine (2 drops) gave the acetoxy sulphide (VIII) (345 mg., 99 *per cent.* yield, m.p. 113.5-114°) which was crystallised from acetone:ethanol, m.p. 114° (Found: C, 52·9; H, 3·8; N, 7·8; S, 9·1. Calcd. for $C_{16}H_{14}N_2O_6S$: C, 53·0; H, 3·9; N, 7·7; S, 8·85%).

Action of acetic acid on 2-chloro-2-phenylethyl 2,4-dinitrophenyl sulphide. The chloro sulphide (VII) (20 g.) in glacial acetic acid (100 ml.) was refluxed for 100 hours. On cooling, β-styryl 2,4-dinitrophenyl sulphide (XI) crystallised (9·1 g., m.p. and mixed m.p. 174·5°). The filtrate was diluted with benzene, washed neutral with water and the dried residue (8·39 g.) chromatographed on silica gel (170 g.) to yield more β-styryl 2,4-dinitrophenyl sulphide (2·5 g., m.p. and mixed m.p. 173-174°) together with tarry eluates from which only trace amounts of the acetoxy sulphide (VIII) could be obtained, sufficient only for a m.p. determination (m.p. 110° with no depression by the pure compound, m.p. 114°).

Formolysis of 2-acetoxy-2-phenylethyl 2,4-dinitrophenyl sulphide. The acetoxy sulphide (VIII) (374 mg.) in formic acid (98 *per cent.*, 5 ml.) was refluxed for 2 hours, yielding a product (300 mg.) of m.p. 148-149°. Crystallisation from acetone gave the pure formyloxy sulphide (XIV), m.p. 151° (Found: C, 51·6, 51·8; H, 3·35, 3·4; N, 8·2. Calcd. for $C_{15}H_{12}N_2O_6S$: C, 51·7; H, 3·5; N, 8·0 %).

The infra-red spectrum in potassium bromide dispersion showed a strong new formate C-O stretching peak[14] at 1168 cm.$^{-1}$.

Reaction of 2,4-dinitrobenzenesulphenyl chloride with styrene in the presence of water. Styrene (5·2 g.) and 2,4-dinitrobenzenesulphenyl chloride (11·73 g.) in *m*-xylene (30 ml.) was refluxed with water (5 ml.) for 8 hours. After working up as before, the reaction product was chromatographed on silica gel (75 g.) yielding as benzene eluate the normal adduct, 2-chloro-2-phenylethyl 2,4-dinitrophenyl sulphide (VII) (11·91g., m.p. and mixed m.p. 141-142°), followed by β-styryl 2,4-dinitrophenyl sulphide (XI) (330 mg., m.p. and mixed m.p. 173-174°). Benzene:ether (1:1) finally eluted 2-hydroxy-2-phenylethyl 2,4-dinitrophenyl sulphide (XIII) (2·10 g., 13 *per cent.* yield, m.p. 128°), crystallising from benzene to m.p. and mixed m.p. 134·5-135° (Found: C, 52·55; H, 4·0; N, 8·8; S, 9·7. Calcd. for $C_{14}H_{12}N_2O_5S$: C, 52·5; H, 3·8; N, 8·75; S, 10·0%).

Thanks are recorded to Mrs. J. M. Snyman for micro-analyses and to Mr. W. C. Botha for preparation of 2,4-dinitrobenzenesulphenyl chloride. Dr. T. J. W. Jorden, the Manager of this Department, is thanked for his interest and for permission to publish this paper.

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THE DETERMINATION OF THE HALF-LIVES AND α-PARTICLE ENERGIES OF SOME RADIOACTIVE ISOTOPES. PART I. THE DETERMINATION OF THE HALF-LIVES OF URANIUM 235 and URANIUM 238

by

F. L. CLARK, H. J. SPENCER-PALMER and R. N. WOODWARD

OPSOMMING

Bepalings word besryf van die halveringstye van U^{235} en U^{238} soos in die jare 1943-1945 deur α-deeltjie-analise van die natuurlike mengsel van uraan isotope vasgestel. Op daardie tydstip was die bestaan van die fyn struktuur van α-deeltjies van U^{235} nog nie bekend nie, maar ons oorspronklike afleidings, nagesien in die lig van huidige kennis, lewer waardes van $7{\cdot}67 \times 10^8$ jaar vir die halvering styd van U^{235} en $4{\cdot}51 \times 10^9$ jaar vir U^{238}.

SUMMARY

An account is given of the determination in 1943-1945 of the half-lives of U^{235} and U^{238} by α-particle analysis of the natural mixture of uranium isotopes. At that time the existence of a fine structure of α-particles from U^{235} had not been established, but correction of our original estimates in the light of present knowledge gives a value of $7{\cdot}67 \times 10^8$ years for the half-life of U^{235} and $4{\cdot}51 \times 10^9$ for U^{238}.

The work described in this paper was undertaken in 1943-1945 and was filed[7] at His Majesty's Stationery Office when it became declassified. Although work on the same subject has since been done by others it was so far as can be ascertained the first successful work of its kind and is therefore presented here for its historic interest. At that time the three natural isotopes of uranium had not been isolated and little was known of the energies of α-particles from U^{235}. It seemed to us that if the α-particles from U^{235} could be resolved by α-particle analysis it would be possible to determine the relative α-particle activities of the three isotopes and hence arrive at estimates of the half-lives of U^{235} and U^{238}.

The work has not been previously published in the scientific literature.

APPARATUS

The α-ray analyser was designed by O. R. Frisch; it consisted of an ionisation chamber and a pulse analyser.

The Ionisation Chamber. The ionisation chamber (Fig. 1) was a vertical cylinder of brass about 16 cm. in diameter and 14 cm. high, closed top and bottom and capable of being evacuated. A horizontal brass slide was used as the sample-holder on which could be placed a platinum disc covered with a thin even layer of the material to be examined. The platinum disc, surmounted by a brass collimator, made electrical contact with the brass slide which in turn was connected with a vertical brass cylinder (No. 1) 11 cm. in diameter projecting upwards; the whole of this assembly was insulated from the remainder of the chamber by polythene and connected to the -900 V tapping of a power pack. Above this cylinder was a brass cap (No. 2) carrying a screen grid of tungsten wire about 0.001 in. in diameter. The assembly was insulated and connected to the -600 V tapping of the power pack. Inside the brass cap was a cir-

cular brass collecting electrode (No. 3) which was insulated and connected to the input of the amplifier.

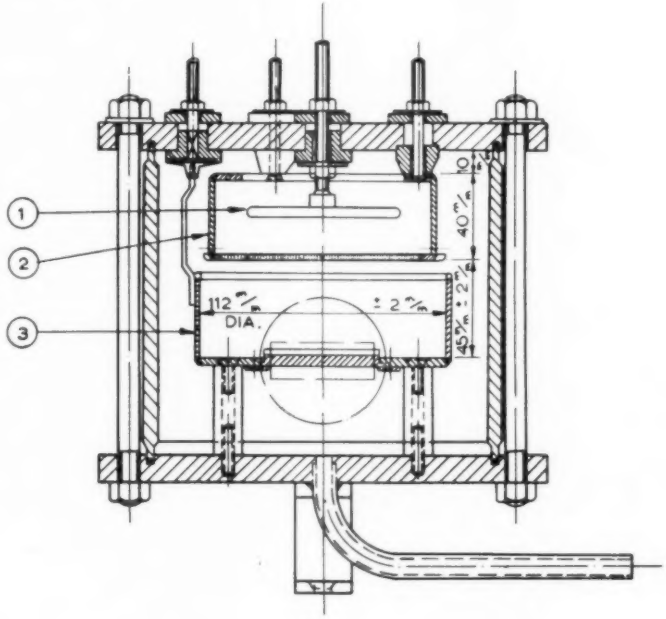

Fig. 1.

After insertion of the platinum disc carrying the sample the chamber was evacuated and filled with dry, oxygen-free argon or nitrogen. The principle of the ionisation chamber was as follows:

α-particles emitted from the sample collided with molecules of argon and ion pairs were produced. The positive ions were attracted back to the cathode and the negative ions (which in this case were electrons) were drawn through the screen grid to the collecting electrode. The distance between the sample and the grid was greater than the range of the α-particles in the gas used so that no ionisation occurred above the grid. The screen grid was designed to protect the collecting electrode against the field from the ions until they had passed through the grid, thus avoiding variation of pulse size with the direction of travel of the α-particle. Some of the electrons were lost to the grid, but these were a contant fraction of the total and the geometry of the grid was such that only a small proportion was lost in this way. The energy of the pulse passed on from the collecting electrode to the amplifier was proportional to the energy of the α-particle.

The Analyser. The analyser consisted of (a) a linear head amplifier, (b) a discriminator/amplifier which amplified the pulses and cut off those lower than a selected voltage and which passed on the fraction of all pulses in excess of this voltage and (c) a pulse analyser in which pulses were recorded on a set of 12 electromagnetic counters, each of which recorded pulses within a given voltage range. In addition,

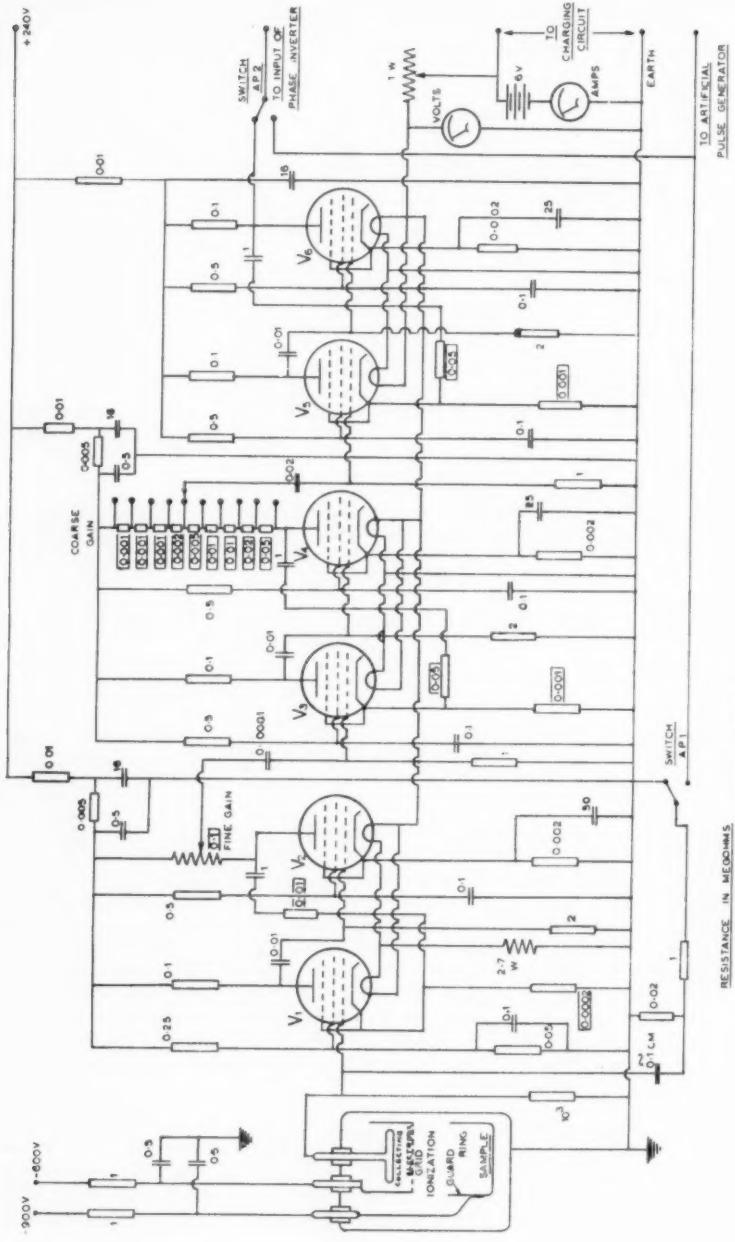
+240V
SWITCH AP2
TO INPUT OF PHASE INVERTER
1 M
VOLTS
TO CHARGING CIRCUIT
6V
AMPS
EARTH
TO ARTIFICIAL PULSE GENERATOR
COARSE GAIN
FINE GAIN
SWITCH AP1
+600V
-900V
COLLECTING ELECTRODE
IONIZATION CHAMBER
GUARD RING
SAMPLE
RESISTANCE IN MEGOHMS
WIRE WOUND RESISTANCES SHOWN THUS 0·002
CONDENSER VALUES IN MICRO FARADS
V1 EF 36
V2 V3 V4 V5 AND V6 EF 50

Fig. 2.

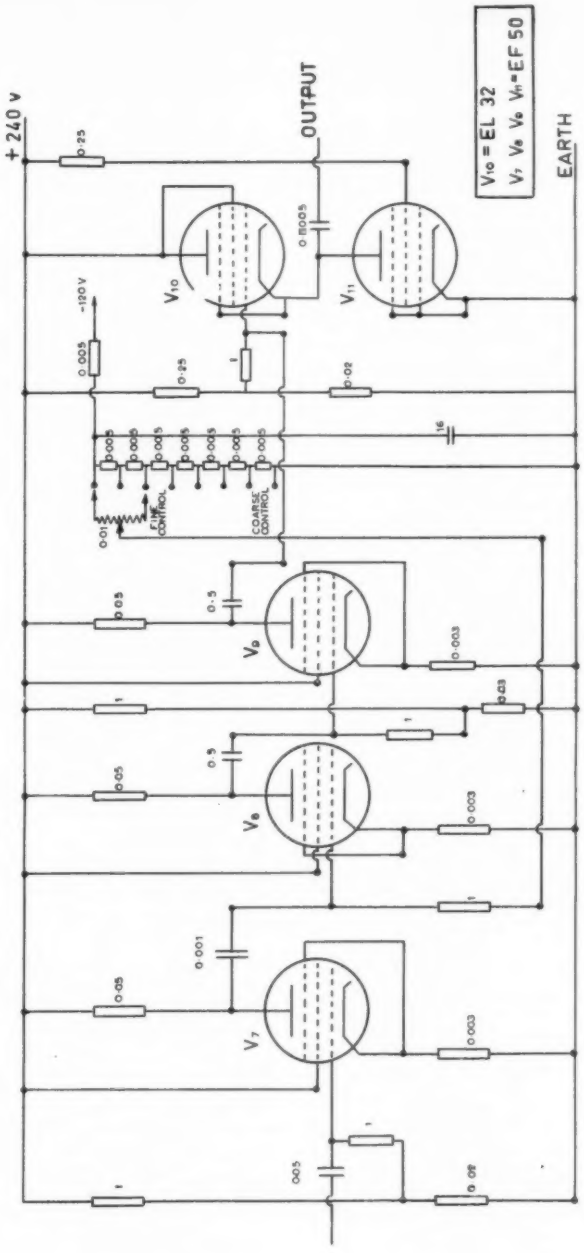
+240 v
OUTPUT
EARTH
V10 = EL 32
V7 V8 V9 V11 = EF 50
-120 V
FINE CONTROL
COARSE CONTROL

Fig. 3.

an artificial pulse generator was provided from which pulses of known voltages could be injected for the purpose of "tuning" the pulse analyser.

At the beginning of the experimental work, great difficulty was experienced in resolving the pulses of U^{234}, U^{235} and U^{238} into three groups. It was then found essential to stabilise H.T. supplies to all valves except those for the screens of the power valves operating the electromagnetic counters and that operating the counters themselves. This was achieved by a control circuit governed by a 100 V accumulator. A stabilised power pack was also particularly necessary for the -120 V bias to the discriminator valve. The L.T. supply to the heaters of all valves in the head amplifier, to the discriminator and to the artificial pulse generator was an accumulator continuously supplied with D.C. current at a rate equal to the load. The E.H.T. supply to the ionisation chamber was adequately controlled by neon stabilisers.

The Head Amplifier. The head amplifier (Fig. 2) consisted of three pairs of valves each of which was provided with negative feed-back. The linearity of the amplifier was satisfactory. To achieve maximum signal/noise ratio a specially selected Mullard EF 36 valve was chosen from a batch for use in the first stage of the amplifier. The grid resistor for this valve ($10^3 M\Omega$) consisted of a glass tube into each end of which was sealed a platinum wire, and the tube was filled with equal volume of toluene and m-nitrotoluene. Electrostatic screening was provided between the various units of the amplifier and the whole was mounted in a steel box containing the chamber itself and protected from vibration by sponge-rubber mountings.

The Discriminator/Amplifier. The discriminator circuit shown in Fig. 3 was satisfactory. V7 was a phase-reversing valve passing a positive pulse to the discriminating valve V8. The bias on the control grid of V8 was controlled by a potentiometer, and this bias voltage determined the cut-off voltage. Pulses from V8 were fed to the phase-reversing valve V9 and thence to valves V10 and V11 which formed a low impedance output feeding the pulse analyser with positive pulses.

The Pulse Analyser. The pulse analyser consisted essentially of thirteen thyratrons operating 12 electromagnetic counters. Each pulse from the discriminator was fed to the control grids of each of the thyratons. The bias voltages on the control grids were fixed beforehand in increasing order of negative voltage, accurately determined by the use of the artificial pulse generator. The principle of the analyser is illustrated by Fig. 4 which gives a simplified circuit. If a positive pulse from the discriminator was large enough to overcome the bias voltages on two contiguous

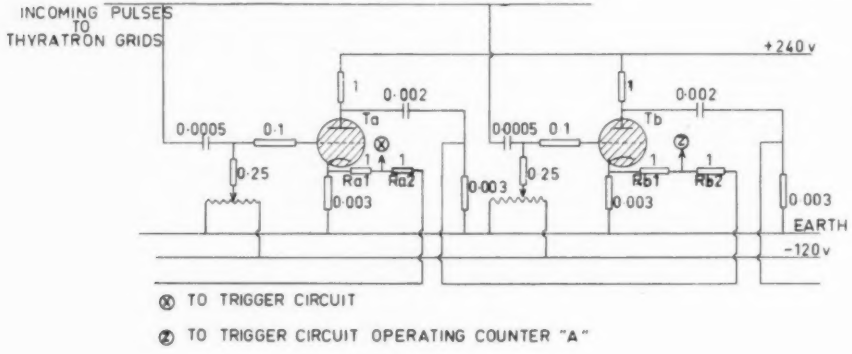

Fig. 4.

thyatrons T_A and T_B, both thyratrons "flashed" (became temporarily conducting). The anode of T_A then passed a negative pulse to resistance R_{B_2} whereas the flashing of T_B sent a positive pulse to R_{B_1}. These positive and negative pulses cancelled out at the point between R_{B_1} and R_{B_2} which therefore remained electrically neutral and did not affect the trigger circuit operating electromagnetic counter A. When both control grids received a pulse which could not overcome the bias voltages of either T_A or T_B, neither thyraton flashed, so that the point between R_{B_1} and R_{B_2} again remained neutral and the counter did not operate. On the other hand, if a given pulse overcame the bias of T_A but not that of T_B, then T_A and all earlier thyratons flashed, but T_B and later thyratons did not. T_A then sent a negative pulse to resistance R_{B_2} but no positive pulse was sent to R_{B_1} by T_B. Hence the point between R_{B_1} and R_{B_2} became negative, and this negative pulse after amplification operated electromagnetic counter A, the only counter operated by the pulse in question.

The "tuning" of the pulse analyser consisted in adjusting the potentiometers supplying bias to the grids of the thyratons. In order to overcome the difficult condition that the characteristic of the discriminator be strictly linear, artificial pulses were fed directly into the discriminator unit and were varied stepwise in equal voltage intervals. This was done by setting the discriminator at a suitable value of cut-off and amplification and then, with the pulse generator step-switch at position 1 (see Fig. 5), adjusting the grid bias potentiometer on thyratron No. 1 until half the artificial pulses were registered on counter No. 1. The step-switch was then turned to position 2 and the bias on thyratron No. 2 adjusted until the pulses were registered equally on counters Nos. 1 and 2. This operation was carried out on the succeeding counters and gave accurate "tuning" because the random variation in pulse size for a given position of the step-switch was small compared with the voltage interval between any two counters. Frequent checks were made of the constancy of the "tuning" and it was found that the characteristics of the analyses were remarkably constant.

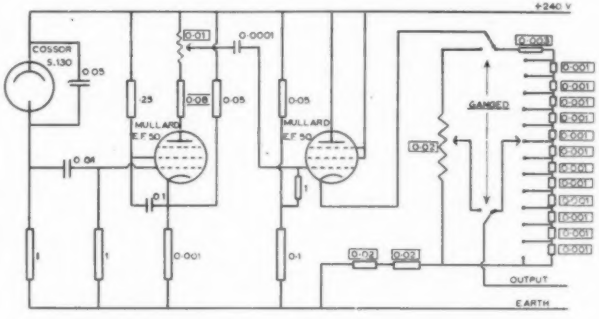

Fig. 5.

EXPERIMENTAL

The primary object of the work was to provide an analytical method for determining the degree of enrichment of U^{235} in isotopic mixtures which had been subjected to a separation process. As far as can be ascertained it had never previously been possible to separate the energy peak of U^{235} α-particles from those of U^{234} and U^{238}, and work was directed at improving the resolution of the three groups. Fig. 6 gives a typical histogram of the frequency-energy relationship observed during

the initial stages, and the lack of resolution is well illustrated. A brief account of the steps taken to improve the technique of α-ray analysis is given below.

Gas used in Ionisation Chamber. Argon as purchased in cylinders contained about 100 p.p.m. of oxygen which had a detectable effect arising from electron capture by oxygen molecules which produced slow-moving negative ions. The gas used was therefore purified to 1 p.p.m. O_2 by adding 0·5 *per cent.* by volume of ammonia, passing through a tube of copper turnings at dull red heat, through a solid CO_2 trap and finally over potassium hydroxide pellets, silica gel and phosphoni oxide.

Increase of gas pressure in the ionisation chamber from 761 mm. mercury to 837 mm. gave no appreciable effect on the histogram, and reduction of pressure produced little effect until the point was reached at which the range of α-particles from U^{234} was equal to the distance from the sample to the screen-grid of the ionisation chamber. It was therefore decided to work at normal atmospheric pressures.

The Ionisation Chamber. Experiments showed that the chamber was insensitive to changes in cathode and grid voltages provided the ratio of these two voltages was approximately constant, in our case at about 1·5. The normal voltages used were -900 V for cathode and -600 V for the grid. The spacing of the wires in the grid had to be sufficiently small to screen the anode effectively but sufficiently large to allow most of the electrons to pass through to the collecting electrode. In our case a spacing of 1 mm. intervals was originally chosen by Frisch, but an increase to 2 mm. produced no appreciable change.

Correction for "blank". Before making any determination, a "blank" determination was carried out on the chamber, and for the conditions used in our work this usually amounted to 3·6 counts/h. for each counter. A deduction was made to allow for this blank, though it represented only a small correction.

Preparation of Samples. For the high resolution required in this work it was necessary to produce a thin even film of the substance under investigation on a disc of platinum in order to minimise self-absorption. In the case of uranium, three different methods were found to be satisfactory, *viz.*:—

(i) The method of Spevack and von Grosse (private communication dated 31st April, 1941) which entailed the use of a solution of a uranium salt in Zapon lacquer.

(ii) A method recommended by the Cavendish Laboratory according to which a salt such as uranyl nitrate was dissolved in pyridine, a suitable small volume placed on the disc which was then warmed to evaporate the pyridine and finally ignited at a dull red heat.

(iii) A method in which a film of U_3O_8 was electro-deposited on the platinum disc which acted as cathode in a cell containing an ammoniacal solution of a uranyl salt together with a large excess of ammonium acetate (which prevented the precipitation of $(NH_4)_2U_2O_7$); the current density was about 1mA./cm^2. When sufficient deposit had been obtained the platinum disc was washed with distilled water and then alcohol after which it was heated to convert the deposit to U_3O_8. This method was a modification of that of Francis and Cheng-da-Chang [1] which when used as described by them gave unsatisfactory results in our experiments.

Of these three methods we found (iii) most satisfactory where the exact weight of deposit was of no consequence, but the Zapon lacquer method was preferable when an exact amount of deposit was required on the disc.

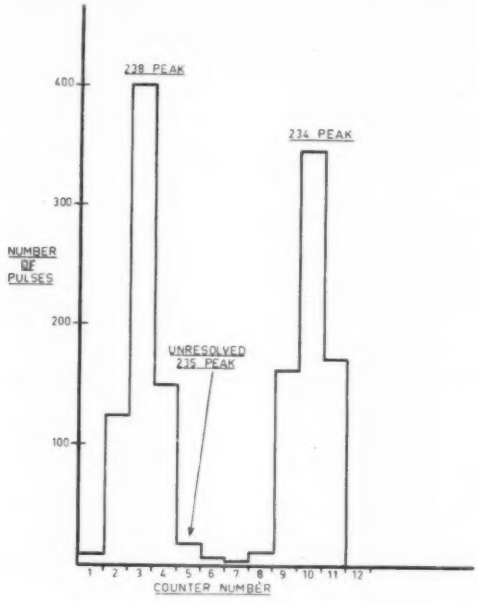
238 PEAK
234 PEAK
UNRESOLVED 235 PEAK
NUMBER OF PULSES
400
300
200
100
1 2 3 4 5 6 7 8 9 10 11 12
COUNTER NUMBER

Fig. 6.

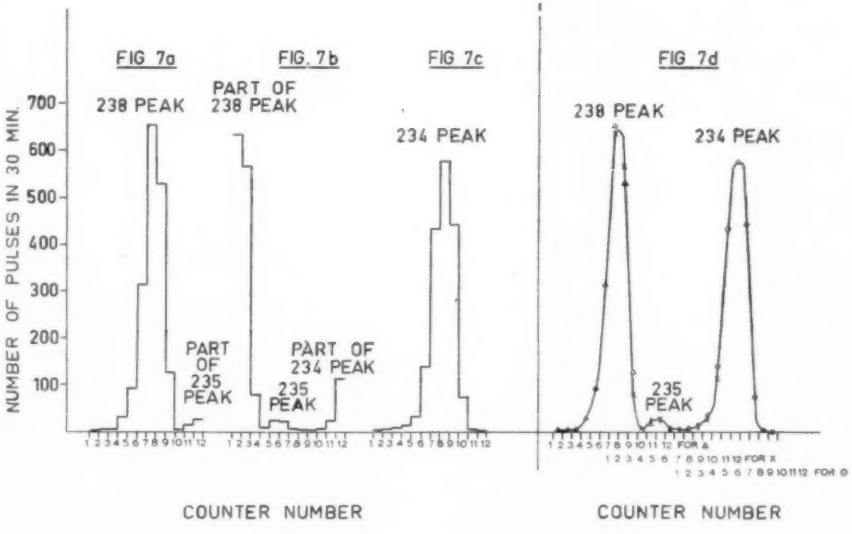
FIG 7a
FIG. 7b
FIG 7c
FIG 7d
238 PEAK
PART OF 238 PEAK
234 PEAK
238 PEAK
234 PEAK
NUMBER OF PULSES IN 30 MIN.
700
600
500
400
300
200
100
PART OF 235 PEAK
235 PEAK
PART OF 234 PEAK
235 PEAK
1 2 3 4 5 6 7 8 9 10 11 12
1 2 3 4 5 6 7 8 9 10 11 12 FOR A
1 2 3 4 5 6 7 8 9 10 11 12 FOR X
1 2 3 4 5 6 7 8 9 10 11 12 FOR ⊙
COUNTER NUMBER
COUNTER NUMBER

Francis[2] has calculated that α-particles from U_3O_8 are completely absorbed by a layer of U_3O_8 14·1μ in thickness. In most of our experiments with uranium the layer was about 0·1μ thick, so that self-absorption was negligible and had very little effect upon the resolution. In this work a collimator which covered the specimens was a disc of brass 4 cm. in diameter, 1·5 mm. thick and perforated with holes 3 mm. in diameter at 3·6 mm. centres; these dimensions were chosen as a compromise to give good collimation without undue reduction of α-particles flux which would have required the use of a thicker layer of U_3O_8 and consequent increase of self-absorption and decrease of resolution.

Accuracy of Tuning of the Analyser. If the tuning of the analyser by the above method was accurate, a continuum of α-particles gave equal numbers of counts on each of the 12 counters. To check this a source was used consisting of a piece of uranium metal 8 mm. square and 2mm. thick; when the amplification was set so that the horizontal plateau of the spectrum was scanned, all the counters gave substantially equal counts.

Loss of Pulses at High Counting Rates. It can be shown that

$$t = \frac{p-r}{pr}$$

where t=resolving time of a counter in min.,
p=number of pulses fed to counter per min.,
and r=number of pulses registered by counter per min.

The above relationship is true if, as in our case, the resolving time of the chamber and amplifier is small compared with that of the counter. If the resolving time t is known then the number of pulses fed to a counter can be calculated for any given rate of recorded pulses. The resolution time of the counters was determined by injecting into one counter (a) regular artificial pulses at a given rate (b) α-particle pulses at a given rate and (c) both the artificial and α-particle pulses at the same rates as in (a) and (b) respectively.

From this the estimated resolution time with a high degree of statistical accuracy was $2{\cdot}88\times10^{-4}$ min., and rearranging the above equation we have

$$p = \frac{r}{1-rt} = \frac{r}{1-2{\cdot}88\times10^{-4}r} \text{ min}^{-1}.$$

This correction was made to the number of pulses recorded on each counter; its effect on the final results was small.

Selection of Amplifier Gain. It can be seen from Fig. 6 that the twelve counters provided on our pulse analyser were inadequate for good resolution of the three groups of α-particles from the natural isotopic mixture of uranium, and the steps taken to improve resolution as described above were insufficient to overcome this handicap. The separation of the peaks in terms of number of counters was proportional to the degree of amplification used, and hence in order to improve resolution by wider separation of the peaks it was necessary to increase the amplification beyond that which gave the result shown in Fig. 6, and indeed to the stage when the whole spectrum of α-particles could not be accommodated by the available 12 counters. The spectrum was therefore analysed in sections (see Fig. 7) taking first the low-energy group of α-particles from U^{238} (Fig. 7A) then the "valley" between U^{238} and U^{234} groups (Fig. 7B) which contained the U^{235} group of α-particles together with the high-energy side of the U^{238} peak and the low-energy side of the U^{234} peak, and finally the high-energy U^{234} group (Fig. 7C). Counts were taken at

constant amplifier gain and the appropriate part of the spectrum was moved on to the 12 counters by means of the discriminator control. It was convenient to move the spectrum along by a known integral number of counters by using artificial pulses as "markers" so that the three sections could be fitted accurately together to give the complete spectrum as in Fig. 7D. The results shown in Fig. 7 are from three half-hour runs, for which the artificial pulse marker method of fitting curves was quite adequate. However, for our determination of the relative α-particle activities of the three uranium isotopes, much longer runs were necessary to give the required statistical accuracy, while the constancy of calibration of artificial pulses could not be relied upon with sufficient exactitude over several days. A graphical method was therefore used to fit the individual sections of the spectrum. For the analysis of the α-particles of the natural uranium isotopes, about 40 separate runs were carried out, each run being first corrected for "blank" counts and for counter loss, after which the graphical fit was made.

RESULTS

Determination of the Half-Life of U^{235}. An α-ray analysis of a natural mixture of uranium was carried out on material prepared from a specimen of highly purified uranyl nitrate, thrice recrystallised from water and finally extracted with ether at the Cavendish Laboratory, to remove thorium isotopes. After making corrections for the "blank" count of the ionisation chamber and for the counter losses, the data were fitted together graphically into the spectrum shown in Fig. 8. Complete resolution of the three groups of α-particles was not obtained, and a device had to be sought for interpreting the results. For this purpose it was assumed that the "tails" of the U^{234} and U^{238} peaks were of the same shape. The shape of the low-energy "tail" of the U^{238} peak was used to derive a "tail" for the low-energy side of the U^{234} peak, and the high-energy "tail" of the U^{234} was used to derive a "tail" for the high-energy side of the U^{238}. These derived "tails" are shown dotted in Fig. 8 and the corrected curves for the U^{238} and U^{234} groups were subtracted from the complete curve to give a curve for the U^{235} peak. Although our results were highly significant statistically, there remained the possibility of some systematic error. The results of four experiments on two samples are given in the following table:—

Sample No.	Expt. No.	Counts/h			Activity ratio	
		U^{238}	U^{235}	U^{234}	U^{234}/U^{238}	$\frac{200 \times U^{235}}{U^{234}+U^{238}}$
1	1A	2726.8 ± 12·4	98.5 ± 0·9	2744·8 ± 13·0	1·007 ± 0·007	3.60 ± 0·07
	1B	2780·9 ± 18·5	101·9 ± 3·4	2773.0 ± 21·8	1·003 ± 0·010	3.67 ± 0·13
2	2A	1001·6 ± 11·8	35·70 ± 1·97	1021·2 ± 11·7	1·020 ± 0·017	3·53 ± 0·20
	2B	1008.3 ± 10·4	38.13 ± 2·13	999·6 ± 11·5	0·991 ± 0·016	3·80 ± 0·20

NOTE.—The errors given above are calculated statistical errors taking into account the error of the "blank" and the error of the counting loss. They do not include any systematic error.

On weighting the above values, the following average values are derived:

$$\frac{\text{Activity } U^{234}}{\text{Activity } U^{238}} = 1{\cdot}005 \pm 0{\cdot}005$$

$$\frac{\text{Activity } U^{235} \times 100}{\text{Average activity of } U^{238} \text{ and } U^{234}} = 3{\cdot}63 \pm 0{\cdot}03 \textit{ per cent.}$$

Kovarick and Adams[3] found that 1 g. of uranium of normal isotopic composition emits a total of 25,010 α-particles per second, and based upon this value, the above

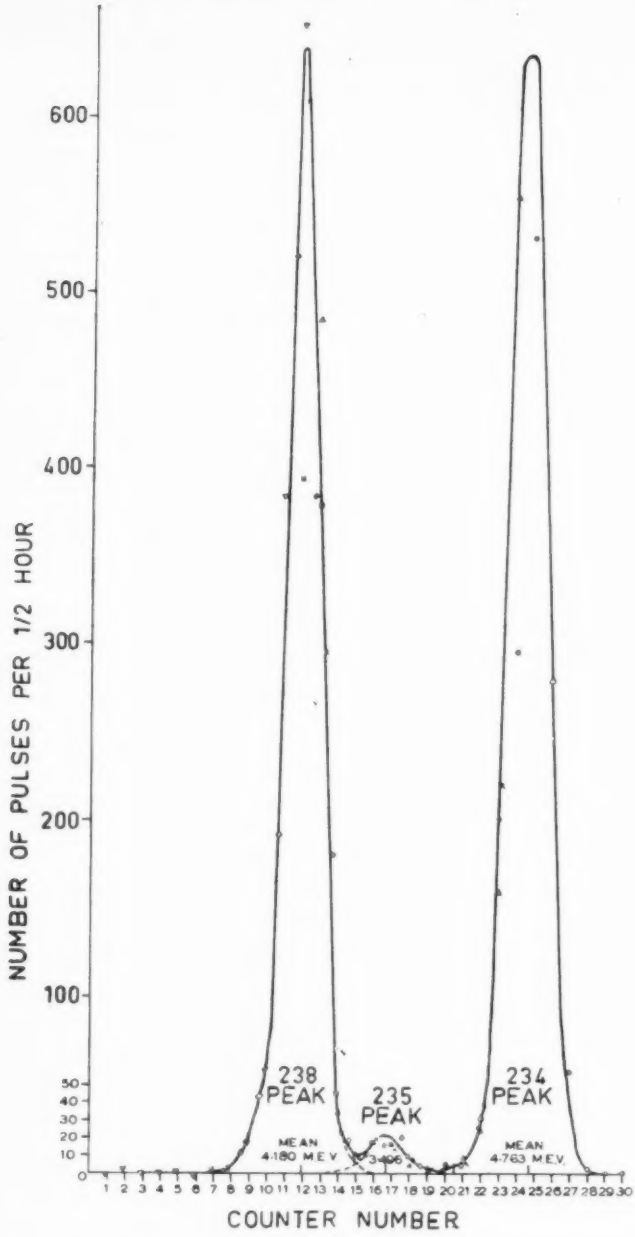
NUMBER OF PULSES PER 1/2 HOUR
600
500
400
300
200
100
50
40
30
20
10
0
238
PEAK
235
PEAK
234
PEAK
MEAN
4·180 M.E.V.
MEAN
4·763 M.E.V.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
COUNTER NUMBER

Fig. 8.

activity ratio of 3·63 gives a value of $8{\cdot}9_1 \times 10^8$ years for the half-life of U^{235} and $4{\cdot}49_8 \times 10^9$ years for the half-life of U^{238}.

DISCUSSION OF RESULTS

The above value of $8{\cdot}9_1 \times 10^8$ years for the half-life of U^{235} was at variance with the only other estimate then available, i.e. that determined by Nier[4] whose method depended upon the isotopic analysis of radiogenic leads which gave a value (also calculated on the basis of the work of Kovarick and Adams) of $7{\cdot}0_6 \times 10^8$ years. Later work by Fleming, Ghiorso and Cunningham[6] gave a half-life of $7{\cdot}13 \times 10^8$ years which is in reasonable agreement with Nier's value. We realised that this discrepancy might be caused by a fine structure of α-particles "lost" in the groups of α-particles of the U^{238} and/or U^{234} groups, as we could find no evidence of another between 3·3 MeV and 5·7 MeV other than the three groups which we had ascribed to the three natural isotopes. Further α-ray analysis of samples which had been enriched with respect to U^{235} and analysed for U^{238} and U^{235} by mass-spectrometry at the Cavendish Laboratory showed that it was not possible to account for the whole of this discrepancy by postulating a U^{235} fine structure group hidden amongst the U^{238} group. One of the remaining possible explanations was that such a fine structure group might have been lost in the U^{234} group but we were unable to check this because the enriched samples were of unknown U^{234} content.

In the light of much more recent work by Ghiorso[5] it now appears that there are four groups of α-particles from U^{235} and these are of such energies as to be hidden in the three groups which we assigned to U^{238}, U^{235} and U^{234} as follows:

MeV	Proportion of total U^{235} α-particles *per cent.*	Hidden in group assigned by us to
4·58	10	U^{234}
4·47	3	U^{235}
4·40	83	U^{235}
4·20	4	U^{238}

If the above results are used to correct our observations we arrive at a value of $7{\cdot}67 \times 10^8$ years for the half-life of U^{235} which is in closer agreement than our previous estimate with Nier's value of $7{\cdot}07 \times 10^8$ and the later value of Fleming, Ghiorso and Cunningham of $7{\cdot}13 \times 10^8$ years.

Similar corrections to our value for the half-life of U^{238} give a value of $4{\cdot}51 \times 10^9$ years which agrees very well with the values of C. A. Kienberger[8] ($4{\cdot}49 \times 10^9$) and Nier ($4{\cdot}51 \times 10^9$).

Thanks are due to O. R. Frisch who designed the original apparatus, to N. Feather for much useful advice and to various workers at the Cavendish Laboratory.

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THE DETERMINATION OF THE HALF-LIVES AND α-PARTICLE ENERGIES OF SOME RADIOACTIVE ISOTOPES. PART II. THE DETERMINATION OF SOME α-PARTICLE ENERGIES

by

F. L. CLARK, H. J. SPENCER-PALMËR and R. N. WOODWARD

OPSOMMING

Verslag word gedoen van die bepaling in 1943-1945 van die α-deeltjie-energieë van U^{234}, U^{235}, U^{238}, Pa^{231}, Th^{228}, Th^{230}, Th^{232} en Ra^{224}. Sommige van hierdie waardes word tans aanvaar en in die "Table of Isotopes" van Hollander, Perlman en Seaborg aangegee; in ander gevalle, waar die voorkoms van fyn struktuur teen daardie tyd nog nie bekend was nie, word ons resultate bevredigend met meer onlangse waardes korreleer.

SUMMARY

An account is given of the determination in 1943-1945 of the α-particle energies of U^{234}, U^{235}, U^{238}, Pa^{231}, Th^{228}, Th^{230}, Th^{232} and Ra 224. Some of these are now amongst the accepted values given in the Table of Isotopes by Hollander, Perlman and Seaborg, and in other cases where the existence of a fine structure was not established at the time, a satisfactory reconciliation of our results with more recent values is made.

As stated in Part I of this paper[1], the work described here was carried out in 1943-1945 and was reported in British Reports which have since been declassified[2]. It is now presented largely for its historical interest, though many of the results are still used together with more recent work where available to arrive at the best values for certain α-particle energies.

At the time when this work was undertaken the determination of α-particle activities was best done by the magnetic deflection method for short-lived isotopes, but this method was unsuited to long-lived elements because of the problem of self-absorption in a source of adequate activity. For this reason the best data then available were based mainly upon range determinations. The determination of α-particle energy by α-ray analysis seemed to provide a much more direct method than that depending on range determinations.

EXPERIMENTAL

The apparatus used was essentially that described in Part I of this paper[1] and in our report of 1944[3]. A new ionisation chamber was, however, used because α-particles from Po^{210} had too long a range for the original chamber; the new chamber had a distance from specimen to grid of 47mm., the optimum chamber voltages being -900 V. and -1500 V.

The method depended on the simultaneous use of Po^{210}, whose α-particle energy was accepted as 5·2984 MeV.[4], and the specimen under investigation. The α-ray analyser was then used to determine the relative pulse sizes of α-particles from Po^{210} and from the specimen, the ratio of those being equal to the ratio of their α-particle energies. The determination of the pulse sizes was carried out as follows:

If V = discriminator bias voltage
P = voltage of pulse entering the discriminator
then x = V+P is a constant of the apparatus for a given counter just to operate.

The discriminator bias voltage required to move a pulse by an accurate interval of 1 counter was determined, using a potentiometer. The value of this at the (constant) amplification used was 0·16 V./counter. In order to find values of x for the individual counters, accurately known fractions of artificial pulses of constant size were fed into the amplifier by means of a calibrated potential divider. By alteration of the discriminator bias the artificial peak for each size of pulse was placed in turn on the same portion of the analyser, the position of the mean peak being determined in each case, and the discriminator voltages being accurately measured. These discriminator voltages were then corrected by the value of 0·16 V./counter to obtain a set of values V_1, V_2 etc. corresponding to pulses P_1, P_2, etc. (whose relative values were of course known) corresponding to precisely the same position on the analyser.

Since $x_1=V_1+P_1=V_2+P_2$ etc. it was possible to derive the best value of x corresponding to various positions on the analyser. The values of x so found were plotted against counter numbers and as expected they fell on a straight line of slope 0·16V./counter. Thus, knowing x from the graph and measuring V it was possible to calculate the pulse voltage P entering the discriminator for a peak on any part of the analyser.

In carrying out an energy measurement relative to Po^{210}, the peak of Po^{210} α-particles was placed on the analyser and the position of the peak and discriminator voltage were accurately determined. The discriminator voltage was then altered to bring the α-particle peak from the other element on to the analyser, again making a determination of the exact mean of the peak and the new discriminator voltage. As a check, the polonium peak was then replaced on the analyser and the determination repeated to ensure that experimental conditions had remained contant. From these data the pulse voltage P for Po^{210} α-particles and those for the element being measured were both determined, and the ratio of the two pulse voltages,

$$\frac{P_1}{P_2}=\frac{V_1-x}{V_2-x}$$ was the energy ratio of the respective α-particles.

The above argument depended upon two assumptions, *viz* :—(a) that the amplifier was linear. This was checked by feeding artificial pulses of known relative sizes into the amplifier and measuring the output pulses from the amplifier by means of a cathode ray oscillograph. The amplifier was linear over a very much wider range of pulse size than was used in the determinations. (b) That the losses of ions in the chamber were a constant fraction of the total number of ions produced. The chief uncertainty was the loss of ions produced in the holes in the collimator. This was resolved by measurement of the α-particle energies of U^{234} and U^{238} both with and without a collimator, which showed no evidence of non-fractional loss of ions.

The polonium used was supplied by the Cavendish Laboratory. The source was prepared by adsorption of polonium from dilute nitric acid solution on a glass microscope cover-slip. The source of the long-lived isotope under investigation was in the form of a thin film on a platinum disc surmounted by a collimator as described in Part I of this paper (*loc. cit.*).

RESULTS AND DISCUSSION

α-Particle energies of U^{234} and U^{238}. The sources used were those described in Part I[1].

The ratios of α-particle energies of U^{234} and U^{238} to the α-particle energy of polonium are given in Table I together with the calculated energies using that of polonium as standard. From these energies the mean ranges in air at 15° and 760mm.

mercury were calculated using the range-energy relationship of Holloway and Livingstone (*loc. cit.* page 31).

TABLE I

α-emitter	Ratio of energy to that of Po^{210}	Energy Mev.	Mean range in air (cm.)
Po^{210}	1·000	5·2984 ± 0·0021	3·842
U^{234}	0·899 ± 0·003	4·763 ± 0·015	3·27 ± 0·02
U^{238}	0·789 ± 0·003	4·180 ± 0·015	2·69 ± 0·02

Table II gives currently accepted values (including ours) taken from the Table of Isotopes of Hollander, Perlman and Seaborg[7]. Our results are in good agreement with those of other workers.

TABLE II

Isotope	Energy MeV	Date	Method	Reference
U^{234}	4·763	1944	ion. ch. *	F. L. Clark *et al.*[2]
	4·76	1939	ion. ch.	J. Schintlmeister *et al.*[6]
	4·76	1951	ion. ch.	A. Ghiorso[8]
	4·78	1937	range air	G. J. Sizoo *et al.*
	4·78	1947	ion. ch.	F. Alder *et al.*
U^{238}	4·180	1944	ion. ch.	F. L. Clark *et al.*[2]
	4·18	1947	ion.ch.	F. Alder *et al.*[10]
	4·21	1939	range	Schintlemeister *et al.*[6]

* "ion. ch." = measurement of pulse sizes in ionisation chamber or proportional counter.

α-Particle energy of U^{235}. The measurement was made in relation not to Po^{210} directly, but to the values of α-particle energies of U^{234} and U^{238} described above. From the work which we had done on the half-life of U^{235} [1] it was convenient to calculate the arithmetic mean for all experiments of the ratios of separation in counters.

$$\frac{\text{Mean of } U^{235} - \text{Mean of } U^{238}}{\text{Mean of } U^{234} - \text{Mean of } U^{238}} = 0{\cdot}3705$$

From this it was deduced that the energy of U^{235} α-particles was 4·396 ± 0·020MeV.

At the time of this determination, the fine structure of α-particles from U^{235} had not been established though in our report[2] we speculated upon the possibility of its existence. It was not possible to investigate this fine structure until substantially pure U^{235} became available since the resolution of the groups was impossible in the normal isotopic uranium samples or even in the enriched samples available at the time.

The more recent work of Ghiorso[8] has established the following α-particle structure:—

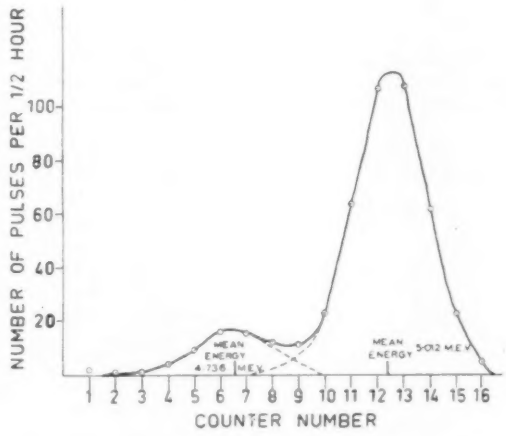
MeV	Relative abundance *per cent.*
4·58	10
4·47 (?)	~ 3
4.40	83
4·20	4

In our measurement, the group of α-particles assigned to U^{235} contained both the 3 *per cent.* of particles of energy 4·47 MeV. and the 83 *per cent.* of energy 4·47 MeV. These two have a weighted mean energy of 4·402 MeV which is in good agreement with our value of 4·396 $\pm$ 0·020 MeV.

α-Particle energy of Po^{231}. The emission of rays from Pa^{231} suggested that its α-ray spectrum was probably complex. A quantity of protoactinium was freed from decay products by the Cavendish Laboratory and given to us as a mixture of Pa and Zr sulphates in dilute nitric acid. A small quantity was deposited on a platinum disc by electrolysis for 16 hrs. at a cathode current density of about 5mA/cm^2. Its α-particle spectrum was investigated in relation to polonium as reference. The results are shown in Fig. 1, from which it can be seen that only two groups were distinguishable, *viz.*:

5·012 $\pm$ 0·015 MeV (87 *per cent.*)
4·736 $\pm$ 0·020 MeV (13 *per cent.*).

FIG 1 α-PARTICLE SPECTRUM OF PROTACTINIUM



These results were in qualitative agreement with the known energies of gamma rays emitted by Pa^{231} (Feather [11]) and were confirmed by subsequent work also using the ionisation chamber method [13], [14]. More recent work by Rosenblum, Cotton and Bouissieres on a magnetic deflection method has shown [12] the presence of the more complex spectrum.

MeV	Abundance *per cent.*
5·042	11
5·002	47
4·938	25
4·838	3
4·720	11
4·660	1—3

In the two groups which we resolved, the higher energy group contained all the α-particles of energies 5·042, 5·002 and 4·938 MeV together with about half those of energy 4·838. The remainder of the α-particles appeared in the low energy group. The weighted mean α-particle energy on this basis was about 4·98 MeV for the higher of the two groups and 4·72 MeV. for the lower. These were in fair agreement with our values of $5{\cdot}012 \pm 0{\cdot}015$ and $4{\cdot}736 \pm 0{\cdot}020$.

α-Particle energy of Ionium (Th^{230}). The sample of ionium used was supplied by the Cavendish Laboratory. The α-particle energy was determined in relation to that of polonium and it was found that

$$^{E}\text{Ionium}/^{E}\text{Polonium} = 0{\cdot}879 \pm 0{\cdot}002$$

whence, taking the energy of polonium α-particles as 5·2984, the energy of ionium α-particles $= 4{\cdot}657 \pm 0{\cdot}011$. This was in good agreement with Geiger's value determined by the range in air method in 1922. A later determination by Rosenblum, Valadares and Vial[15] using the magnetic deflection method, revealed a fine structure of α-particles as follows:—

MeV	
4·682	(~75 *per cent.*)
4·613	(~25 *per cent.*)
4·51	(?)

This fine structure ws not resolved in our α-ray analysis but the weighted average of Rosenblum's α-particle energies for the particles of energy 4·682 and 4·613 is 4·66, which is in excellent agreement with our results and the earlier ones of Geiger.

The α-ray spectrum of Thorium (Th^{232}, Th^{230}, Th^{228} and Ra^{224}). A source was prepared from B.D.H. thorium nitrate mounted on a platinum disc by the Zapon lacquer method. It carried 0·72 mg. ThO_2 and was used with a collimator consisting of perforated zinc sheet 0·4 mm. thick with 2·0 mm. holes hexagonally spaced at 3·0 mm. centres.

It was not possible to use polonium as the direct reference standard owing to interference with the Th^{228} (Radiothorium) group of α-particles. Instead, the ionium group of α-particles was used as the standard since the energy of these had been determined as described in the previous section of this paper. The ionium group of particles from the thorium source was confirmed as in fact due to ionium by carrying out an experiment in which both a thorium source and an ionium source were simultaneously placed in the chamber. The α-particle spectrum is shown in Fig. 2.

To identify with greater certainty the group of α-particles assigned to Ra^{224}, a sample of thorium was purified from Ra^{224} by precipitating thorium hydroxide with ammonia from a nitric acid solution, redissolving in nitric acid and repeating the process eight times. The time of final separation was noted, the purified thorium hydroxide converted to nitrate from which a source was prepared, and the sample was examined in the ionisation chamber as soon as possible. It was left in the chamber and the spectrum was examined eight times over an interval of 14 days. The growth of the high energy peak (5·661 MeV.) confirmed our assignment of this to Ra^{224} and further confirmation was supplied by the rate of growth which was consistent with the known half-life of Ra^{224} (3·64 days).

The following energies were derived on the basis of our value of $4{\cdot}657 \pm 0{\cdot}011$ MeV for α-particles from ionium:—

α-emitter	Energy (MeV)
Th^{232}	$3{\cdot}976 \pm 0{\cdot}020$
Th^{228} (Radiothorium)	$5{\cdot}383 \pm 0{\cdot}020$
Ra^{224} (Thorium x)	$5{\cdot}661 \pm 0{\cdot}020$

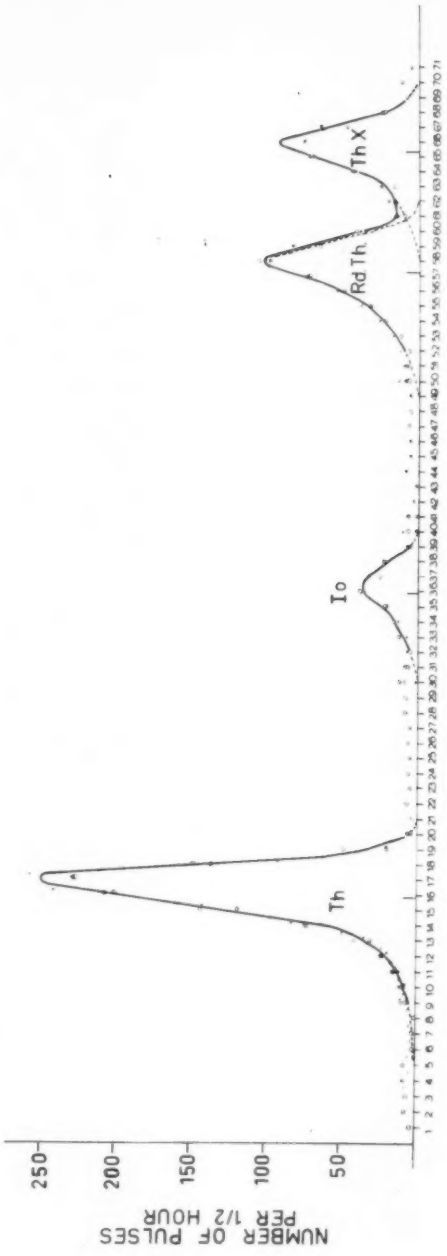

NUMBER OF PULSES PER 1/2 HOUR
250
200
150
100
50
Th
Io
Rd Th
Th X
COUNTER NUMBER

Fig. 2.

The following table is abstracted from the Table of Isotopes[7] which gives the accepted values for comparison with our own.

α-Emitter	Energy Mev	Date	Method*	Reference
Th^{232}	3·98	1945	ion. ch.	F. L. Clark *et al.*[2]
	3·98	1951	range emulsion	H. Faraggi[16]
	4·20	1937	ion. ch.	J. Schintlmeister[17]
Th^{228}	5·423 (72%)	1949	spect.	S. Rosenblum *et al.*[18]
	5·338 (28%)			
Ra^{224}	5·681 (95 %)	1949	spect.	S. Rosenblum *et al.*[19]
	5·448 (4·6%)			
	5·194 (0·4%)			
	5·681	1936	spect.	G. H. Briggs
	5·66	1945	ion.ch.	F. L. Clark *et al.*[2]

*Abbreviations:—"ion. ch."=measurement of pulse sizes in ionisation chamber or proportional counter; "spect."=magnetic deflection.

Our value of 3·976 for Th^{232}, rounded off to 3·98 MeV, is apparently accepted as the best value. Our results of $5{\cdot}383 \pm 0{\cdot}020$ for Th^{228} is not listed in the above table as one of the acceptable values, but it is in agreement with the best value given. Our apparatus was unable to resolve the two groups of α-particles consisting, according to Rosenblum *et al.*, of 5·423 (72 *per cent.*) and 5·338 (28 *per cent.*). The weighted average of these two groups is 5·40 which agrees with our value within the error claimed.

Our value of $5{\cdot}661 \pm 0{\cdot}020$ for Ra^{224} is rounded off to 5·66 and included in the table as an acceptable value. Here again our apparatus could not resolve the fine structure as could Rosenblum's magnetic deflection method, but the latter gives a weighted average of 5·668 which is in good agreement with our figures.

Thanks are due to O. R. Frisch who designed the original apparatus, to N. Feather for much useful advice, and to various workers at the Cavendish Laboratory.

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